

## Steam reforming of tar compounds over Ni/olivine catalysts doped with CeO<sub>2</sub>

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### Abstract

Biomass gasification is gaining attention as a route for biomass energy production. Producer gas from this process usually contains unacceptable levels of tar. Tar can cause operational problems in downstream processes by blocking gas coolers, filter elements and engine suction channels. Most producer gas applications require removal of at least part of the dust and tar before the gas can be used.

In this study, olivine was used as a substrate for various catalyst formulations designed to steam reform tar to gas. Three catalysts were prepared by wet impregnation, yielding the following compositions: 3.0% NiO/olivine, 3.0% NiO/olivine doped with 1.0% CeO<sub>2</sub> and 6.0% NiO/olivine. Benzene and toluene were selected as model compounds of biomass tar. Catalytic steam reforming of these compounds was performed in a bench scale fixed bed reactor at temperatures between 700 and 830 °C using a molar ratio of steam/carbon (S/C) equal to 5. The effect of catalyst composition on tar conversion and yields of various product gases were determined. Coking tendencies of the catalysts were determined, and characterization by XRD and SEM was performed. 3.0% NiO/olivine doped with 1.0% CeO<sub>2</sub> was the most promising catalyst based on catalytic activity and its resistance to coking.

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### 1. Introduction

Biomass as a source of renewable energy has several environmental advantages over fossil fuels. The main advantage is the lower net emission of greenhouse gases. Gasification of biomass produces a raw gas mixture composed of hydrogen (H<sub>2</sub>), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O), methane (CH<sub>4</sub>) and various light hydrocarbons. The producer gas also contains several undesirable constituents, including dust (ash and char), ammonia (NH<sub>3</sub>), alkali (mostly potassium), sulfur, chlorine and tar. Tar is a complex mixture of aromatics including a significant fraction of polycyclic aromatic hydrocarbons. The concentrations of gas impurities are 5–30 g/Nm<sup>3</sup> for particulate matter [1] and 0.5–30 g/Nm<sup>3</sup> for volatile alkali

metals, depending on the type of gasifier and the characteristics of the feedstock. Tar content varies from 5 to 75 g/Nm<sup>3</sup> for fluidized bed gasifiers [2–4]. This range is well above the maximum allowed for gas turbines and diesel engines [1,5], so most power applications require substantial removal of tar before the gas can be used.

Tar cracking and reforming increases the gas heating value and the overall efficiency of the biomass thermochemical conversion process. This approach is more desirable than water or oil scrubbing to remove tar, which poses environmental hazards not easily resolvable.

Both manufactured catalysts and naturally occurring minerals known to promote tar cracking and reforming have been investigated for potential incorporation in the gasification process [6]. Although the former are undoubtedly needed to reach very stringent specifications on gas purity, there is abundant experimental evidence that inexpensive and widely available basic oxide minerals are

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effective in drastically reducing the tar content of producer gas [7]. In fact, simple mineral oxides are often suggested for initial gas conditioning followed by a secondary catalytic reactor in which the gas composition is further refined [8].

It is well known that dolomite efficiently decomposes tar at the operating conditions usually employed in gasification processes [9,10]. Dolomite has been utilized directly in fluidized bed gasifiers as well as in secondary reactors [11] in both demonstration units and industrial installations [12]. The main problem with dolomite is its friability, which causes it to disintegrate into fines, which pose problems for the stable operation of the fluidized bed gasifier and its ancillary units.

For economic reasons, nickel catalyst is the most suitable choice among metals like cobalt (Co), iron (Fe), platinum (Pt), ruthenium (Ru) and rhodium (Rh). Several nickel (Ni) based catalysts have been investigated and found to be very effective in terms of tar removal [13–15]. Ni based catalysts are also very effective for ammonia (NH<sub>3</sub>) removal [16,17]. The main limitation in using Ni based catalysts is severe deactivation of the catalyst. This deactivation occurs mainly when the catalyst is placed immediately after the gasifier where high tar levels cause coking and trace contaminants poison the catalyst. Steam reforming catalysts are useful for polishing purposes when very clean gas is needed in such operations as Fischer–Tropsch reactions.

Most commercially available Ni catalysts display moderate to rapid deactivation due to the build up of surface carbon and ‘sintering’ effects [18]. This latter phenomenon occurs at high temperatures. When nickel is deposited on a support (usually alumina), the metallic particles tend to migrate and form larger aggregates, reducing the dispersion and consequently the catalyst activity. Sintering also encourages the formation of coke.

Olivine is a mineral containing magnesium oxide, iron oxide and silica. Olivine is resistant to attrition compared to dolomite. Investigations by Rapagna et al. [19] showed that olivine’s activity in steam reforming of tar was superior to that of calcined dolomite. The authors also performed experiments with olivine as bed material with lanthanum–nickel–iron (La–Ni–Fe) tri-metallic perovskite catalyst in a secondary reactor. The combined action of these materials was very promising; a gas with around 0.3 g /m<sup>3</sup> of tar was obtained [20]. Rose’n et al. [21] reported success in using olivine as bed material for pressurized gasification (0.4–1.0 MPa) of birch. However, Abu El-Rub et al. [22], using naphthalene as a model tar compound, observed no significant catalytic activity for olivine. Other researchers have proposed the use of olivine as a catalyst support [23,24].

Olivine contains iron, which helps stabilize nickel in the support structure [25,26]. The initial nickel–olivine interactions have to be strong enough to prevent nickel sintering and attrition of the active phase. Moreover, to be active for methane (CH<sub>4</sub>) reforming, nickel particles must be accessible. Nickel strongly linked to the olivine support

has previously been suggested for use with fluidized bed gasifiers [24]. The results of previous research have revealed that the characteristics of natural olivine (hardness, density and basicity) would be of particular interest in respect of this application. Active phase support interactions affect the dispersion of transition metals and the catalytic activity of the catalysts prepared from them [27,28]. Che and Bonnevot [29] have developed a two step preparation method capable of controlling the particle size of Ni/SiO<sub>2</sub> catalyst. The nucleation step gave nickel oxide nuclei in strong interaction with the support; thereby the impregnation step effectively yielded a nickel reservoir [30]. The effects of the active phase composition (Ni and/or NiO) are considered in relation to the catalytic properties in the dry reforming of methane (CH<sub>4</sub> + CO<sub>2</sub>) [31].

Cerium oxide (CeO<sub>2</sub>) has been used as a promoter in Ni based catalysts to enhance the resistance to coke formation since the Ni–CeO<sub>2</sub> system has strong metal support interaction [32]. The role of CeO<sub>x</sub> ( $x = 2$  or  $1.5$ ) is to accelerate the reaction of steam with absorbed gaseous species on the nickel surface near the boundary area, so that carbon appearing on the surface can be quickly converted to gaseous products, preventing its accumulation. An attractive solution will be to associate nickel and olivine with cerium oxide as a promoter because olivine has an appropriate structure and mechanical strength. Moreover, olivine contains iron that can help stabilizing nickel in the structure [25,26]. Cerium oxide can improve catalytic activity and resistance to coking. The integration of small amounts of nickel into natural olivine could control the reducibility of nickel oxide and prevent carbon deposition on the catalyst during either dry or steam reforming of methane [33]. This paper is an investigation of NiO/olivine and NiO/olivine doped with CeO<sub>2</sub>. Benzene and toluene were used as model tar compounds to evaluate the catalytic quality and resistance to carbon deposition of the synthesized catalysts during steam reforming.

## 2. Experimental procedures

### 2.1. Micro-reaction system

A schematic of the experimental apparatus, which employs a WFS-3010 micro-reaction system manufactured by Xian Quan Science and Technology Ltd, Tianjin, China, is shown in Fig. 1. Hydrogen (H<sub>2</sub>) and nitrogen (N<sub>2</sub>) were metered into a stainless steel vessel that served in these experiments to heat the gas mixture to 600 °C. Mass flow meters adjusted the gas flow in the range of 10–200 ml/min. Liquid pumps were used to inject a model tar compound (benzene or toluene) and water into the gas flow, where they quickly evaporated at the elevated temperature, with metering accuracy better than 1.0%. Benzene and toluene injection rates were 1.7 ml/h. and 1.8 ml/h, respectively. The steam to carbon (S/C) ratio was maintained at 5.0. The hot gas mixture was admitted into a catalytic reactor constructed of a quartz tube with internal

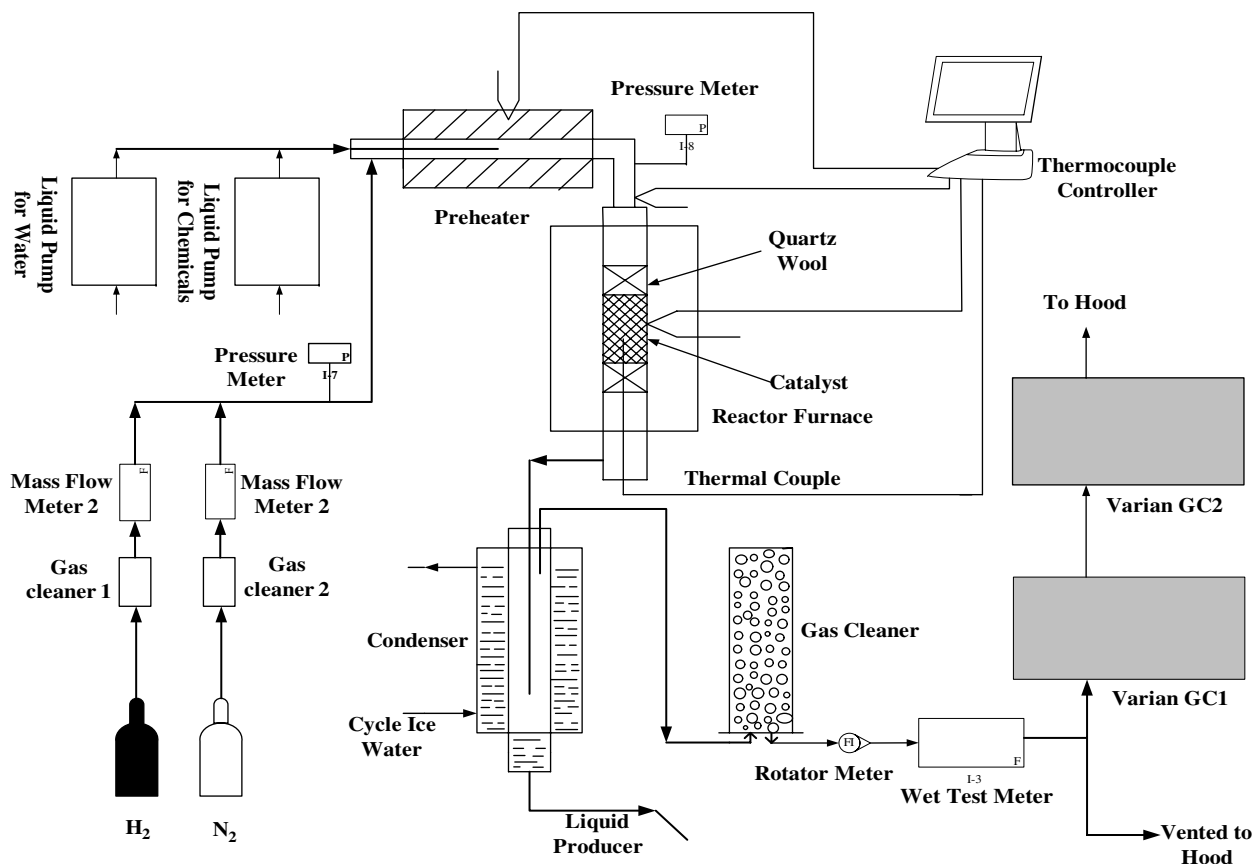


Fig. 1. The schematic diagram of the reaction system.

diameter of 8 mm and length of 280 mm. The catalytic reactor was mounted inside an electric furnace, which had a large homothermal area compared to the reactor dimensions. Temperatures were measured with two 1.0 mm OD thermocouples (type K), one placed at the center of the catalyst bed in the tubular reactor and the other placed against the outside surface of the tubular reactor wall. A pressure gage monitored the pressure drop across the catalyst bed during tests. Gases and vapors exiting the tubular reactor were passed through an ice water condenser where non-converted fractions of the model tar compounds were substantially condensed. Traces of steam and benzene were absorbed in a gas cleaner prior to analysis of the gas stream. A rotameter monitored the flow rate of product gas during a test, while a wet test meter monitored the cumulative volume of gas exiting the reactor.

The composition of the gas mixture at the reactor exit was determined by two on line Varian Model CP-3380 gas chromatographs (GC) with thermal conductivity detectors (TCD) with detection limits of 2 ppm and linear dynamic range of  $10^4$ . One GC was equipped with a Molsieve 5A column and a thermal conductivity detector with argon as carrier gas to measure  $H_2$ ,  $O_2$ ,  $N_2$ ,  $CH_4$  and CO. The GC was equipped with a Porapak Q column and a thermal conductivity detector with helium as carrier gas to measure carbon dioxide ( $CO_2$ ) and ethylene ( $C_2H_4$ ). This system performed a complete gas analysis every 7 min.

The duration of each test was 1 h with average gas composition calculated from the approximately eight measurements made during a test. The cumulative volume was monitored by a wet test meter so that the total volume of producer gas and the average volumetric flow rate at standard temperature and pressure (STP) could be calculated.

Conversion of model tar compounds to gaseous products ( $CO$ ,  $CO_2$  and  $CH_4$ ) in the presence of the different catalysts was determined as a function of temperature ( $T$ ), steam to carbon ratio ( $S/C$ ) and space velocity ( $SV$ ). Conversion efficiency,  $\eta$ , was calculated using the expression:

$$\eta = 100Q(F_{CO} + F_{CO_2} + F_{CH_4}) / (M \times N_C) \quad (1)$$

where  $Q$  is the volumetric flow rate of gas (l/h);  $F_{CO}$  is the mole fraction of carbon monoxide in the gas products;  $F_{CO_2}$  is the mole fraction of carbon dioxide in the gas products;  $F_{CH_4}$  is the mole fraction of methane in the gas products;  $N_C$  is the molar feed rate of carbon to the reactor (mol/h); and  $M$  is the molar density of the gas (22.4 mol/l).

## 2.2. Catalyst materials and preparation

The catalysts were prepared in the laboratory by wet impregnation. Preparation method, chemical composition and surface areas for the catalysts are listed in Table 1. The nickel and cerium contents are expressed as weight

Table 1  
The chemical composition, preparation and surface areas for the catalysts

Catalyst	Preparation technique	Composition (wt%)	Specific area (m <sup>2</sup> /g)	Pore radius (Å)
Olivine carrier	Natural mine	MgO 49.0, SiO <sub>2</sub> 42.0 Fe <sub>2</sub> O <sub>3</sub> 8.0, Al <sub>2</sub> O <sub>3</sub> 0.5, CaO 0.5	4.55	21.23
A	One impregnation	NiO 3.0% on olivine carrier	1.26	68.24
B	Two impregnations	NiO 3.0% CeO <sub>2</sub> 1.0% on olivine carrier	2.16	36.01
C	Two impregnations	NiO 6.0% on olivine carrier	2.31	52.81

percent in the synthesized catalysts. Olivine supports were from Xixia Heqiang Company, China. The as received natural olivine was crushed and sieved to particle sizes between 20 and 30 mesh. Ni(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O and Ce(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O were dissolved in de-ionized water. Nickel and cerium were loaded onto supports by wet impregnation with Ni(NO<sub>3</sub>)<sub>3</sub> and Ce(NO<sub>3</sub>)<sub>3</sub> solutions, respectively, followed by drying in a vacuum at 105 °C for 8 h. After drying, the samples were calcined in air at a low heating rate until a final calcination temperature of 800 °C was achieved and maintained for 2 h. Three catalysts were obtained: 3.0%NiO/olivine, 3.0%NiO/olivine doped with 1.0%CeO<sub>2</sub> and 6.0%NiO/olivine, which are subsequently referred to as catalyst A, catalyst B and catalyst C, respectively.

### 2.3. Catalytic testing

The synthesized catalysts were sieved to particle sizes between 20 and 30 mesh in order to minimize internal mass transfer limitations [4]. Catalyst in the amount of 0.5 ml was loaded into the reactor for each test. A small plug of quartz wool at the bottom and top of the catalyst bed held the catalyst in place. A thermal couple placed at the center of the bed monitored reaction temperature. The gas preheater was heated to 600 °C, and the catalyst bed was heated to 700 °C while passing 100 ml/min N<sub>2</sub> through it. Prior to starting a test, the catalyst was reduced at 700 °C by flowing a mixture of 50% H<sub>2</sub> and 50% N<sub>2</sub> through the reactor at a rate of 80 ml/min for 2.5 h. To commence a test, gas flow through the reactor was stopped and the catalyst bed was brought to the desired temperature. When the temperature stabilized, the model tar compound (either benzene or toluene) and steam were injected into the preheater where they were rapidly vaporized. The steam reforming of benzene and toluene were performed at the operating conditions specified for each test. Measurements included reactor pressure drop, volumetric flow rate and total gas volume exiting the reactor and gas composition (via the GC). During the steam reforming tests, space velocities were chosen high enough to minimize external mass transfer limitations while holding conversion efficiencies less than 80% (higher conversion efficiencies were not easily resolved in the present experimental system).

### 2.4. Catalyst characterization

Fresh and used catalysts were analyzed by powder X-ray diffraction (XRD), which was performed with a Japan D/Max-3B type diffractometer with a CuK $\alpha$  radiation source.

Operating conditions were 2 $\theta$  between 10° and 70°, current set to 30 mA and scan rate of 6°/min. The diffraction patterns were identified by comparing them with those listed in the Joint Committee of Powder Diffraction Standards (JCPDS) data base [34]. Specific area and pore structure of the fresh and used catalysts were measured by BJH mode, which was performed with a US NOVA1000e Surface and Pore Analyzer. Scanning electron microscopy (SEM) was performed with a Japan Electronic JSM-5610LV SEM with accelerating voltage 0.5–30 kV and electron flow 1 pA–1  $\mu$ A and equipped with an energy spectrum analyzer.

## 3. Results and discussion

### 3.1. Catalyst for steam reforming

The baseline operating condition was initially selected to be the benzene injection rate of 3.6 ml/h (3.18 g/h), ICI steam reforming commercial catalyst volume 0.5 ml, S/C ratio equal to 5.0, space velocity (SV) equal to 1826 h<sup>−1</sup> and reactor temperature equal to 750 °C. However, within 115 min of starting tests under these conditions, the reactor became clogged by coke as indicated by a dramatic increase in pressure drop across the reactor. Thus, it was necessary to redefine the baseline test to be a benzene injection rate equal to 1.7 ml/h (1.5 g/h), catalyst volume equal to 0.5 ml, space velocity equal to 862 h<sup>−1</sup> and S/C ratio equal to 5. The baseline test for toluene had similar operating conditions except that the toluene injection rate was 1.8 ml/h. All subsequent catalysts tests were performed under these baseline conditions.

### 3.2. Performance of NiO/olivine catalysts

Tables 2–5 summarize the gas product compositions upon steam reforming of benzene and toluene for the three synthesized catalysts at 700 °C, 750 °C, 800 °C and 830 °C, respectively. Generally, the gas products are 60–64 vol% H<sub>2</sub>, 17–33 vol% CO, 4–18 vol% CO<sub>2</sub> and less than 0.2 vol% CH<sub>4</sub>. All three impregnated catalysts of olivine catalyzed benzene steam reforming. The mechanism of steam reforming involves the absorption of the target molecules and water vapor on the catalyst surface where they react until all carbon atoms are converted to CO or CO<sub>2</sub>. Methane is not a reaction intermediate or primary product and must be formed from CO through the methanation reaction. However, methanation is clearly unimportant as methane was less than 0.2% of the product gases.

Table 2

Gaseous products from steam reforming of benzene and toluene for three catalyst formulations (A, B and C) at 700 °C (catalyst volume of 0.5 ml; S/C ratio = 5.0; SV = 862 h<sup>-1</sup>)

Catalyst	Benzene steam reforming				Toluene steam reforming			
	H <sub>2</sub> (%)	CH <sub>4</sub> (%)	CO (%)	CO <sub>2</sub> (%)	H <sub>2</sub> (%)	CH <sub>4</sub> (%)	CO (%)	CO <sub>2</sub> (%)
A	62.39 ± 0.12	0.02 ± 0.01	32.33 ± 0.27	5.26 ± 0.29	63.44 ± 0.42	0.09 ± 0.02	24.37 ± 1.68	12.10 ± 1.72
B	64.00 ± 0.29	0.02 ± 0.01	23.90 ± 0.91	12.09 ± 1.15	64.84 ± 0.64	0.11 ± 0.01	16.60 ± 0.90	18.45 ± 1.33
C	63.55 ± 0.12	0.04 ± 0.01	31.66 ± 0.27	4.74 ± 0.29	63.88 ± 1.05	0.15 ± 0.02	23.63 ± 1.45	12.33 ± 0.29

Note: Uncertainty in tabulated values is expressed as 95% confidence intervals.

Table 3

Gaseous products from steam reforming of benzene or toluene for three catalyst formulations (A, B and C) at 750 °C (catalyst volume of 0.5 ml; S/C ratio = 5.0; SV = 862 h<sup>-1</sup>)

Catalyst	Benzene steam reforming				Toluene steam reforming			
	H <sub>2</sub> (%)	CH <sub>4</sub> (%)	CO (%)	CO <sub>2</sub> (%)	H <sub>2</sub> (%)	CH <sub>4</sub> (%)	CO (%)	CO <sub>2</sub> (%)
A	61.26 ± 0.37	0.01 ± 0.00	32.47 ± 1.10	6.26 ± 1.14	61.32 ± 0.21	0.16 ± 0.02	28.85 ± 0.14	10.17 ± 0.22
B	63.61 ± 0.56	0.01 ± 0.01	23.82 ± 0.29	12.55 ± 0.52	63.61 ± 0.35	0.11 ± 0.01	22.49 ± 0.65	14.63 ± 0.76
C	61.94 ± 0.37	0.01 ± 0.00	31.64 ± 1.10	6.42 ± 1.14	61.15 ± 0.41	0.22 ± 0.02	29.29 ± 0.48	9.35 ± 0.12

Note: Uncertainty in tabulated values is expressed as 95% confidence intervals.

Table 4

Gaseous products from steam reforming of benzene and toluene for three catalyst formulations (A, B and C) at 800 °C (catalyst volume of 0.5 ml; S/C ratio = 5.0; SV = 862 h<sup>-1</sup>)

Catalyst	Benzene steam reforming				Toluene steam reforming			
	H <sub>2</sub> (%)	CH <sub>4</sub> (%)	CO (%)	CO <sub>2</sub> (%)	H <sub>2</sub> (%)	CH <sub>4</sub> (%)	CO (%)	CO <sub>2</sub> (%)
A	61.97 ± 0.21	0	33.27 ± 0.23	4.75 ± 0.28	58.13 ± 1.69	0.16 ± 0.03	31.18 ± 1.19	10.53 ± 0.54
B	63.44 ± 0.41	0	27.57 ± 0.52	8.99 ± 0.52	61.83 ± 0.44	0.20 ± 0.02	23.41 ± 0.36	14.56 ± 0.29
C	62.84 ± 0.21	0	29.83 ± 0.23	7.33 ± 0.28	58.88 ± 0.28	0.17 ± 0.02	31.62 ± 0.21	9.33 ± 0.20

Note: Uncertainty in tabulated values is expressed as 95% confidence intervals.

Table 5

Gaseous products from steam reforming of benzene and toluene for three catalyst formulations (A, B and C) at 830 °C (catalyst volume of 0.5 ml; S/C ratio = 5.0; SV = 862 h<sup>-1</sup>)

Catalyst	Benzene steam reforming				Toluene steam reforming			
	H <sub>2</sub> (%)	CH <sub>4</sub> (%)	CO (%)	CO <sub>2</sub> (%)	H <sub>2</sub> (%)	CH <sub>4</sub> (%)	CO (%)	CO <sub>2</sub> (%)
A	61.61 ± 0.40	0	28.54 ± 0.80	9.85 ± 0.63	58.88 ± 0.81	0.13 ± 0.03	31.00 ± 1.05	9.99 ± 0.47
B	62.50 ± 0.36	0	26.54 ± 0.69	10.96 ± 0.65	60.61 ± 0.24	0.29 ± 0.03	25.22 ± 0.36	13.87 ± 0.40
C	61.74 ± 0.40	0	30.31 ± 0.80	7.94 ± 0.63	59.57 ± 1.45	0.17 ± 0.04	33.53 ± 1.00	10.73 ± 0.73

Note: Uncertainty in tabulated values is expressed as 95% confidence intervals.

Fig. 2(a)–(d) plot H<sub>2</sub> concentration vs. benzene or toluene conversion for steam reforming by the synthesized catalysts at 700 °C, 750 °C, 800 °C and 830 °C, respectively. As shown by the figures, catalyst A produced hydrogen to the same extent as catalyst C. Benzene or toluene conversions for catalyst A were slightly higher than the conversions for catalyst C at the four temperatures. This indicates that the catalytic activities of catalysts A and C were almost the same despite the 3.0%Ni difference in their catalyst compositions. Catalyst B produced more hydrogen than catalysts A and C. Benzene or toluene conversions for catalyst B were much higher than the conversions for catalysts A and C at 700 °C, 750 °C and 800 °C, respec-

tively. However, at the highest temperature tested (830 °C), the differences in conversion were not obvious. Apparently, catalyst B, which was the CeO<sub>2</sub> doped 3.0%NiO/olivine, had better catalytic performance than catalyst A, the 3.0%NiO/olivine and catalyst C, the 6.0%NiO/olivine. In other words, the doped CeO<sub>2</sub> promoted the catalytic property of the NiO/olivine catalyst.

### 3.3. Comparison of NiO/olivine catalysts with NiO/olivine doped with CeO<sub>2</sub> catalyst

Benzene conversion was compared for 3.0%NiO/olivine (catalyst A), 3.0%NiO/olivine doped with CeO<sub>2</sub> (catalyst



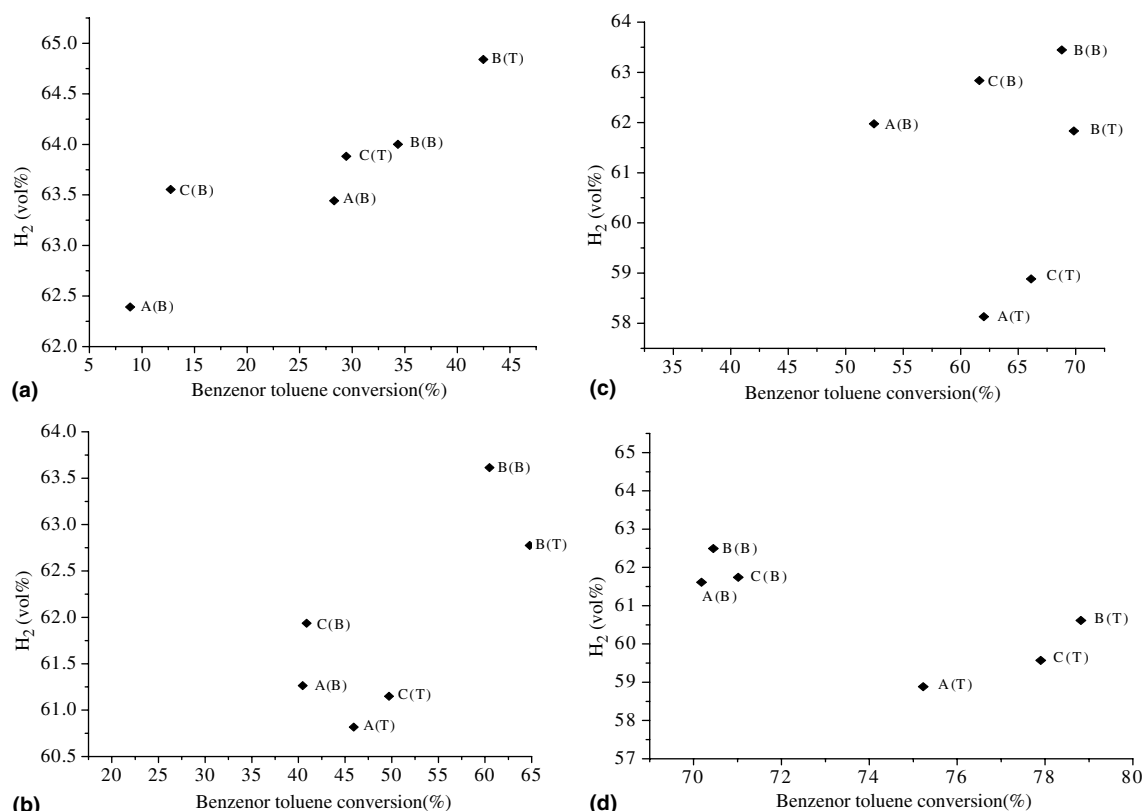


Fig. 2.  $H_2$  concentration vs. benzene (B) or toluene (T) conversion for steam reforming of benzene using three catalyst formulations (A, B and C). Conditions were: catalyst volume of 0.5 ml; S/C ratio = 5.0; SV = 862 h<sup>-1</sup>; reaction temperature (a) 700 °C; (b) 750 °C; (c) 800 °C; (d) 830 °C.

B) and 6.0%NiO/olivine (catalyst C). Benzene steam reforming tests were performed at 700 °C, 750 °C, 800 °C and 830 °C, respectively. Table 6 illustrates the effect of temperature on benzene conversion among the three catalysts. At 700 °C, the benzene conversions by catalysts A, B and C were 5.26%, 34.4% and 12.7%, respectively. At 750 °C, the benzene conversions by catalysts A, B and C were 40.5%, 60.5% and 40.9%, respectively. At 800 °C, the benzene conversions by catalysts A, B and C were 52.4%, 68.8% and 61.6%, respectively. At the higher temperature 830 °C, the benzene conversions by catalyst A, B and C were 70.2%, 70.4% and 71.0%, respectively. For all three catalysts, the benzene conversions increased with temperature increase. Benzene conversions by catalyst B were much higher than those by catalysts A and C at lower temperature. At the highest temperature (830 °C), the

difference was less than one half percent. This clearly indicated the reaction was controlled by chemical equilibrium. NiO/olivine doped with CeO<sub>2</sub> had better catalytic activity than NiO/olivine for benzene steam reforming. Table 2 also illustrates that the catalysts produced CH<sub>4</sub> less than 0.04% at temperature 700 °C and about 0.01% at the temperature 700 °C. At higher temperature, product CH<sub>4</sub> was so small as to be undetectable.

Table 7 illustrates the effect of temperature on toluene conversion among the three catalysts. Although the trend for these results is similar to those obtained for benzene, toluene conversion was higher than benzene conversion at comparable reaction conditions. This result is not surprising as benzene has a more stable chemical structure than toluene. For all three catalysts, toluene conversions increased with temperature increase. Toluene conversions

Table 6

Benzene conversion and  $H_2$  and CH<sub>4</sub> concentrations for steam reforming of benzene: comparison of synthetic catalysts A, B and C

$T$ (°C)	Benzene conversion (%)			$H_2$ (vol%)			CH <sub>4</sub> (vol%)		
	A	B	C	A	B	C	A	B	C
700	5.26	34.4	12.7	62.4 ± 0.12	64 ± 0.29	63.6 ± 0.12	0.02 ± 0.01	0.02 ± 0.01	0.04 ± 0.01
750	40.5	60.5	40.9	61.3 ± 0.37	63.6 ± 0.56	61.9 ± 0.37	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
800	52.4	68.8	61.6	62 ± 0.21	63.4 ± 0.41	62.8 ± 0.21	0	0	0
830	70.2	70.4	71	61.6 ± 0.4	62.5 ± 0.36	61.7 ± 0.4	0	0	0

Note: Uncertainty in tabulated values is expressed as 95% confidence intervals.

by catalyst B were much higher than those of catalysts A and C at lower temperatures. At the higher temperature of 830 °C, toluene conversions for catalyst A, B and C were 75.2%, 78.8% and 77.9%, respectively. The difference

became smaller with temperature increase and was within 1.0% at the temperature of 830 °C. This clearly indicates the reaction was controlled by chemical equilibrium at temperature 830 °C. NiO/olivine doped with CeO<sub>2</sub> had better

Table 7

Toluene conversion and H<sub>2</sub> and CH<sub>4</sub> concentrations for steam reforming of toluene: comparison of synthetic catalysts A, B and C

<i>T</i> (°C)	Toluene conversion (%)			H <sub>2</sub> (vol%)			CH <sub>4</sub> (vol%)		
	A	B	C	A	B	C	A	B	C
700	28.3	42.5	29.4	63.4 ± 0.42	64.8 ± 0.64	63.9 ± 1.05	0.09 ± 0.02	0.11 ± 0.01	0.15 ± 0.02
750	45.9	64.8	49.7	61.3 ± 0.21	63.6 ± 0.35	61.1 ± 0.41	0.16 ± 0.02	0.1 ± 0.01	0.22 ± 0.02
800	62	69.8	66.1	58.1 ± 1.69	61.8 ± 0.44	58.9 ± 0.28	0.16 ± 0.03	0.2 ± 0.02	0.17 ± 0.02
830	75.2	78.8	77.9	58.9 ± 0.81	60.6 ± 0.24	59.6 ± 1.45	0.13 ± 0.03	0.29 ± 0.03	0.17 ± 0.04

Note: Uncertainty in tabulated values is expressed as 95% confidence intervals.

Table 8

Carbon content of three expended catalysts

Catalyst	A		B		C	
	Carbon content (wt%)	On stream (h)	Carbon content (wt%)	On stream (h)	Carbon content (wt%)	On stream (h)
Sample 1 <sup>a</sup>	13.8 ± 3.1	10	2.4 ± 0.7	10	15.2 ± 3.3	10
Sample 2 <sup>b</sup>	14.6 ± 2.8	8	3.2 ± 0.8	10	18.0 ± 3.4	8

Note: Uncertainty in tabulated values is expressed as 95% confidence intervals.

<sup>a</sup> Used for benzene steam reforming.

<sup>b</sup> Used for toluene steam reforming.

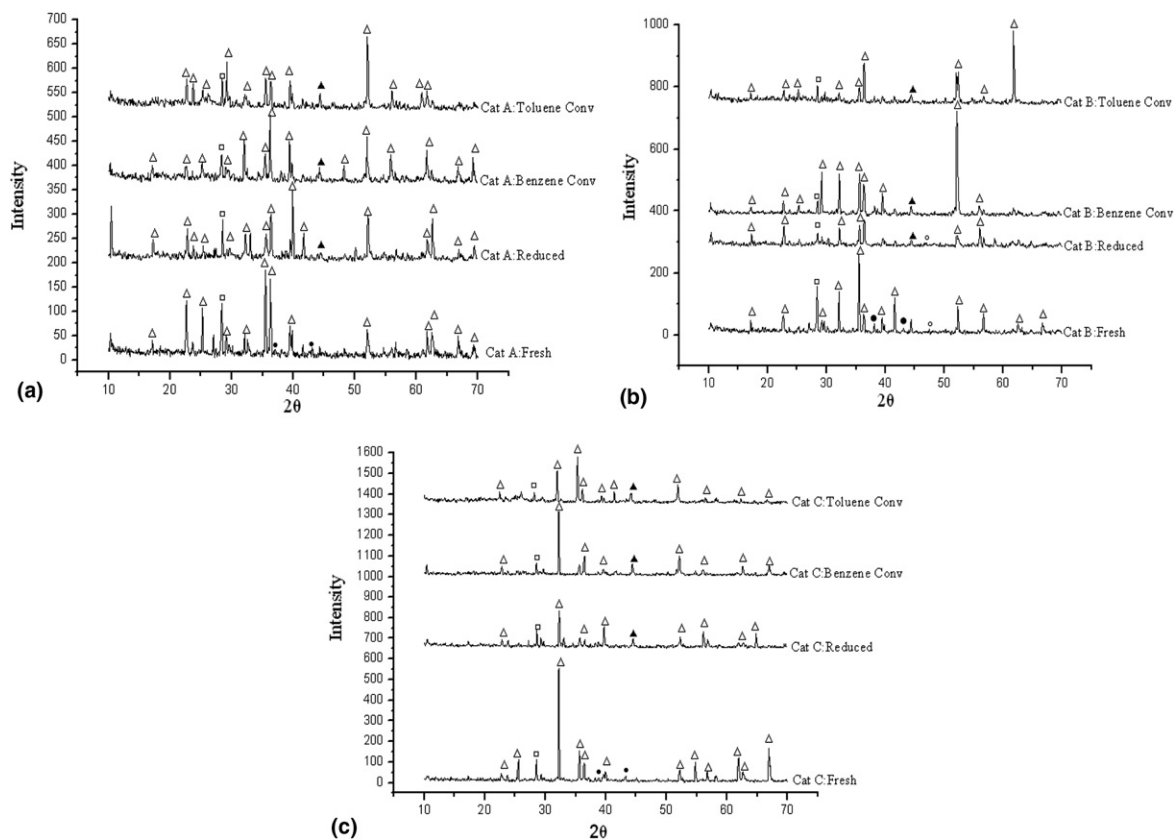


Fig. 3. X-ray diffraction (XRD) of synthesized catalysts. (a) Catalyst A, (b) catalyst B and (c) catalyst C (peaks: ▲ – Ni, ● – NiO, ○ – CeO<sub>2</sub>, △ – Mg<sub>2</sub>SiO<sub>4</sub>, □ – (Mg, Fe)SiO<sub>3</sub>).

catalytic activity than NiO/olivine for toluene steam reforming. Table 3 also illustrates that the catalysts produced  $\text{CH}_4$  of less than 0.3%, which was much higher than that from benzene steam reforming at the same reaction conditions.

Table 8 shows the carbon content by elemental analysis of the three expended catalysts. The amount of carbon found on catalysts A and C, on the order of 15 wt%, was much higher than the amount of carbon found on catalyst B, which was only about 3 wt%. These values indicated that doped  $\text{CeO}_2$  could improve the resistance to carbon deposit on the Ni/olivine catalyst.

### 3.4. Characterization by XRD and SEM

Fig. 3(a)–(c) illustrate the crystal phases of the fresh, pre-reduced and expended catalysts A, B and C, respectively. The fresh NiO/olivine catalysts were composed of NiO,  $\text{Mg}_2\text{SiO}_4$  and  $(\text{Mg, Fe})\text{SiO}_3$  according to the JCPDS file of the  $\text{Mg}_2\text{SiO}_4$  [34,35]. Besides the peaks of NiO/

olivine catalyst, there was a very small  $\text{CeO}_2$  peak in the NiO/olivine doped  $\text{CeO}_2$  catalyst. In the reduced and expended samples, nickel appeared instead of NiO. Metallic nickel was an active component, while  $\text{CeO}_2$  was a promoter for the steam reforming catalyst.

Fig. 4(a)–(d) illustrate the scanning electron micrographs (SEM) of the reduced catalysts and expended catalysts. The catalysts look similar before and after testing. This similarity suggests that the principal effect of the catalytic test is the reduction of nickel oxide particles to the metal along with an accompanying decrease in size. For the catalyst obtained via a two step impregnation by nickel and cerium, the change consists of a less regular distribution of the metal upon the surface.

Table 9 shows the surface elemental compositions of reduced and expended catalysts A and B. Surface carbon content was much higher on the used NiO/olivine catalyst than on the used doped  $\text{CeO}_2$  NiO/olivine catalyst. Surface oxygen content was much higher on the used NiO/olivine catalyst than on the used doped  $\text{CeO}_2$  NiO/olivine catalyst.

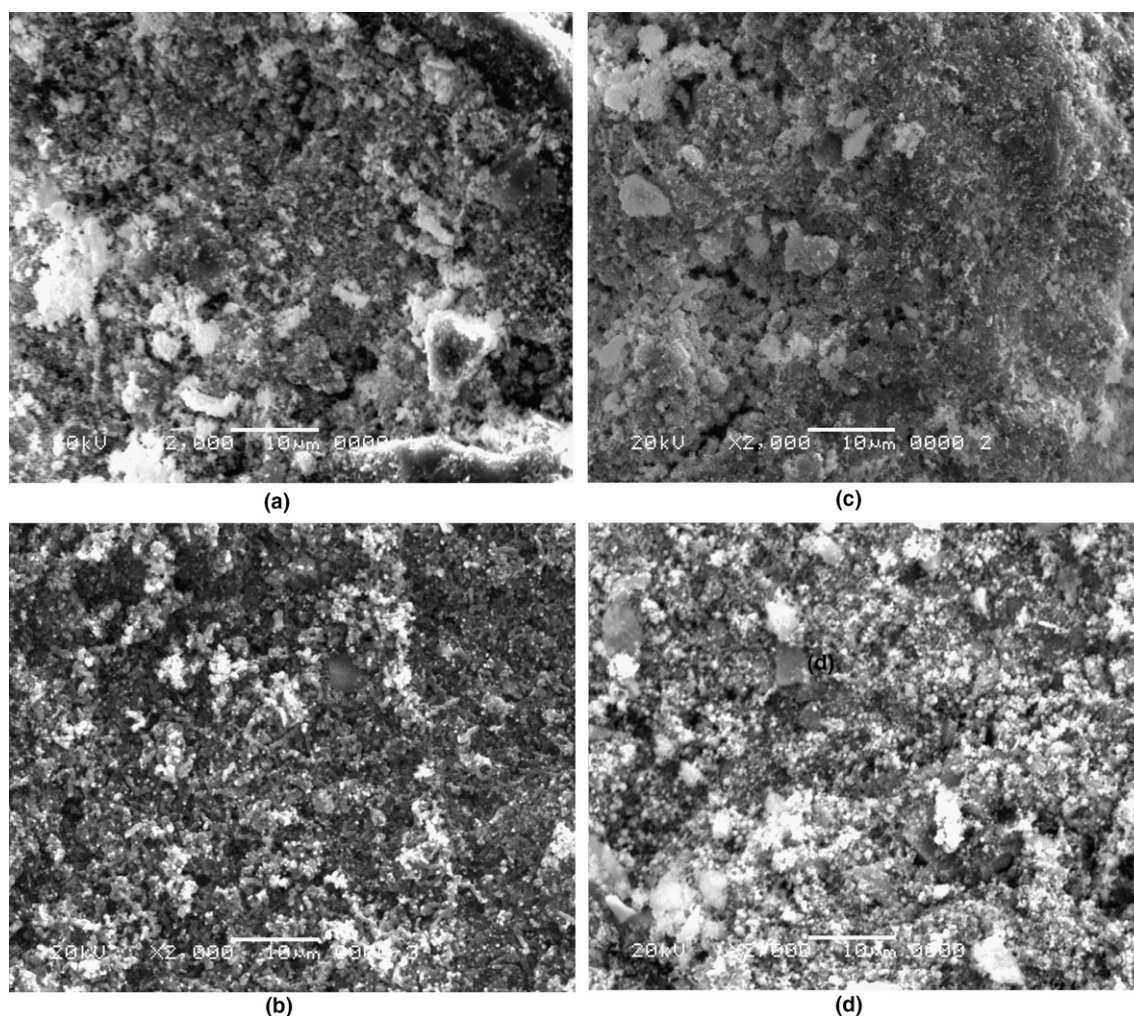


Fig. 4. Scanning electron micrographs of catalysts: (a) Reduced 3.0% Ni/olivine, (b) used 3.0% Ni/olivine, (c) reduced and (d) used 3.0% Ni/olivine doped with 1.0% Ce.



Table 9  
Surface composition of catalysts

Catalyst	Elemental composition (wt%)						
	Mg	Si	Fe	O	Ni	Ce	C
Reduced A	8.3 ± 4.2	4.4 ± 2.2	3.1 ± 1.6	5.5 ± 2.8	70.7 ± 35.4	0	8.0 ± 4.0
Used A	5.9 ± 3.0	5.5 ± 2.8	1.2 ± 0.6	6.8 ± 3.4	11.1 ± 5.6	0	69.5 ± 24.8
Reduced B	10.1 ± 5.1	6.3 ± 3.2	4.6 ± 2.3	5.9 ± 3.0	50 ± 25.0	16.1 ± 8.1	7.0 ± 3.0
Used B	8.9 ± 4.5	11.9 ± 6.0	1.9 ± 1.0	14 ± 7.0	32.4 ± 16.2	4.7 ± 2.4	26.2 ± 13.1

Note: Uncertainty in tabulated values is expressed as 95% confidence intervals.

Doped CeO<sub>2</sub> improved the properties and increased the crystal oxygen on the surface, which benefited the redox reaction during the steam reforming.

Carbon deposition on catalysts has been widely studied [36,37]. The tendency of carbon to deposit depends upon the nature and fate of surface carbon species. The carbon species can either react with water or form products (hydrogen, carbon monoxide and carbon dioxide) or pass through a series of steps leading to carbon deposition. The carbon deposition process can be regarded as a competitive reaction with steam reforming. A general approach to preventing coke accumulation includes both reducing the deposition rate and increasing the rate of carbon gasification. Hydrocarbon steam reforming is an oxidative dehydrogenation process: the hydrocarbons are oxidized by steam to form carbon monoxide and carbon dioxide and simultaneously give up hydrogen. In the doped CeO<sub>2</sub>-NiO/olivine catalyst, some of the cerium might be in the state of Ce(III) during the steam reforming process. The cerium oxide promoting effect is assumed to be via a redox mechanism. The lower valence state cerium might adsorb water and dissociate it, the resulting species –O or –OH transferring to nickel and reacting with surface carbon species to form CO, CO<sub>2</sub> and H<sub>2</sub>.

#### 4. Conclusions

Natural olivine showed good performance as a support for nickel catalysts. The hardness, density and basicity are compatible with the gasification environment. A proportion of nickel oxide is included in the olivine and maintains the level of reducible nickel oxide.

Steam reforming of benzene and toluene were investigated for Ni/olivine and Ni/olivine doped with CeO<sub>2</sub> catalysts. NiO/olivine doped with CeO<sub>2</sub> catalyst was particularly effective compared to the other two NiO/olivine formulations (catalysts A and C) in terms of both catalytic activity and coking resistance.

Cerium oxide is thought to promote the catalytic activity of nickel and resist the deposition of the carbon. CeO<sub>x</sub> ( $x = 1.5$  or  $2$ ) produced during the catalyst reduction, which also existed in the steam reforming environment. The promotion effect of cerium oxide on the nickel catalyst for steam reforming of benzene is probably through a redox mechanism. The lower valence state cerium might adsorb water and dissociate it, the resulting species –O or

–OH transferring to the nickel and reacting with surface carbon species to form carbon monoxide, carbon dioxide and hydrogen.

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